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A Convenient Preparation of Acylsulfenyl Bromides: A New Class of Electrophilic Thiocarboxylating Agents

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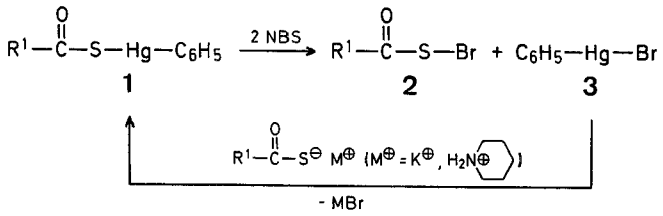
Thiocarboxylation has been generally effected by the use of nucleophilic reagents such as alkali or alkali earth metal thiocarboxylates. In contrast, acylsulfenyl halides are potential electrophilic thiocarboxylating reagents (Umpolung synthon). However, due to their instability these compounds have rarely been investigated[1]. We now report the first successful preparation and isolation[2] of acylsulfenyl bromides **(2)** (Table 1) from the reaction of phenylmercury thiocarboxylates **(1)** with *N*-bromosuccinimide (NBS) (Scheme **A**).

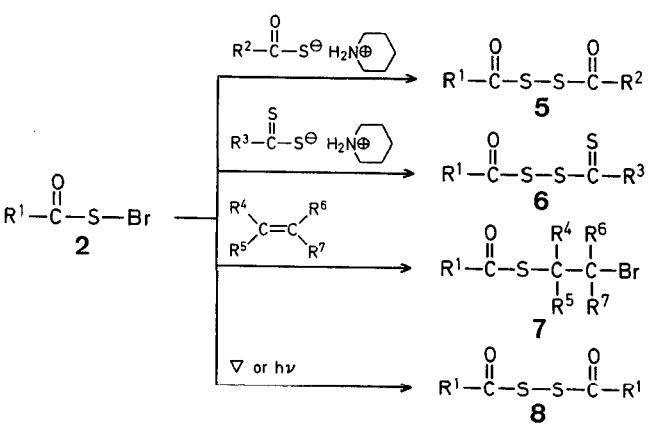


Scheme **A**

The phenylmercury bromide **(3)** simultaneously formed is readily and almost quantitatively reconverted into the educt **1** by reaction with piperidinium or potassium thiocarboxylates.

The acylsulfenyl bromides **2** were characterized by spectral data and by microanalyses. For example, the mass spectrum of **2a** shows molecular ions at $m/e = 216$ and 218. The I.R. spectrum shows a characteristic absorption band at 1686 cm^{-1} due to the C=O stretching frequency. Its position differs distinctly from that of the corresponding band of the educt **1a** ($R^1 = C_6H_5$, $\nu_{C=O} = 1629$ cm^{-1}) and from that of bis[benzoyl] disulfide ($\nu_{C=O} = 1703$ and 1684 cm^{-1}), the possible decomposition product.

Compounds **2** react with piperidinium thio- and dithiocarboxylates to give the corresponding unsymmetrical disulfides **5**[3] or **6**[4] and with alkenes to give the addition products **7** (Scheme **B**).



Scheme **B**

The acylsulfenyl bromides **2** obtained are stable for 2-3 h at room temperature, both in the solid state and in solution (methanol or *n*-hexane); however, they decompose when heated over their melting point or exposed to sun light, yielding free bromine and the corresponding symmetrical disulfides **8**.

Benzoylsulfenyl Bromide (2a); Typical Procedure:

To a suspension of phenylmercury thiobenzoate[5] (**1a**; 207 mg, 0.5 mmol) in chloroform (30 ml) is added *N*-bromosuccinimide (178 mg; 1 mmol). The reaction mixture is stirred for 30 min at room temperature. The colorless solution turns to pale yellow within 15 min and a white solid precipitates. The solvent is evaporated below 20 °C under reduced pressure and then *n*-hexane (20 ml) is added. After removal of the insoluble white solid (phenylmercury bromide and succinimide) by filtration, the filtrate is allowed to stand at ~ −70 °C for 1 h. Filtration of the resulting solid and recrystallization from *n*-hexane gives pure **2a** as pale yellow needles; yield: 92 mg (85%); m.p. 50–53 °C (dec.).

C_7H_5BrOS	calc.	C 38.73	H 2.32
(217.1)	found	38.33	2.31

I.R. (KBr): $\nu = 1686$ cm^{-1} (C=O).

Benzoyl 4-Methylbenzoyl Disulfide (5a; $R^1 = C_6H_5$, $R^2 = 4\text{-}H_3C\text{—}C_6H_4$); Typical Procedure:

A solution of potassium thiobenzoate (176 mg, 1 mmol) in dichloromethane (20 ml) is added dropwise to 4-methylbenzoylsulfenyl bromide (231 mg, 1 mmol) in the same solvent (15 ml) at −78 °C. After stirring for 15 min, dichloromethane (50 ml) is added, the mixture is washed with 10% sodium hydrogen sulfate solution (10 ml), and then water (3 × 10 ml). After drying with sodium sulfate, evaporation of the solvent in vacuo and subsequent recrystallization of the resulting residue from petroleum ether (b.p. <40 °C) gives **5a** as colorless crystals; yield: 254 mg (88%); m.p. 89–90 °C (Ref.[3], m.p. 89–90.5 °C).

Benzoyl Thiobenzoyl Disulfide (6a; $R^1 = R^3 = C_6H_5$); Typical Procedure:

Benzoylsulfenyl bromide (**2a**; 108 mg, 0.5 mmol) in methanol (20 ml) is added dropwise to piperidinium dithiobenzoate[6] (120 mg, 0.5 mmol) in the same solvent (30 ml) and the mixture is stirred at room temperature for 1 h. The resulting precipitate is filtrated and then dissolved in dichloromethane (50 ml), followed by washing with 10% sodium hydrogen sulfate solution (10 ml) and then water (3 × 10 ml). After evaporation of the solvent, the resulting residue is chromatographed on silica gel [Wako Gel-200, dichloromethane/*n*-hexane (1:4)] to give **6a** as reddish violet crystals; yield 88 mg (62%); m.p. 65–67 °C (Ref. [4], m.p. 63–67 °C).

***S*-(2-Bromocyclopentyl) 4-Methylbenzenethiocarboxylate (7c); Typical Procedure:**

A solution of cyclopentene (75 mg, 1.1 mmol) in dichloromethane (5 ml) is added to 4-methylbenzoylsulfenyl bromide (**2c**; 120 mg, 0.52 mmol) in the same solvent (15 ml) at −70 °C and the mixture is stirred for 30 min. After removal of the solvent in vacuo, the residue-containing dichloromethane (~1 ml) is separated by preparative T.L.C. [Wako Gel B-5F, *n*-hexane/ether (10:1)] to give **7a** as colorless needles; yield: 140 mg (90%); m.p. 37–39 °C.

$C_{12}H_{15}BrOS$	calc.	C 52.18	H 2.32
(299.2)	found	52.20	2.39

I.R. (KBr): $\nu = 1658$ cm^{-1} (C=O).

^{1}H-N.M.R. ($CDCl_3$): $\delta = 1.51$–2.84 (m, 6H, CH_2); 2.37 (s, 3H, CH_3); 4.08–4.50 (m, 2H, CH); 7.06–7.80 ppm (m, 4H, Ar).

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Bis[benzoyl] Disulfide (8a); Typical Procedure:
Benzoylsulfenyl bromide (**2b**; 217 mg, 1 mmol) is exposed to sunlight at room temperature for 15 min to give **8a** as a colorless solid; yield: 215 mg (99%); m.p. 132 °C.

I.R. (KBr): $\nu = 1703$, 1684 cm^{-1} (C=O).

Table. Acylsulfenyl Bromides **2** prepared

Product No.	R^1	Yield [%]	m.p. [°C][a]	Molecular formula[b]	I.R. (KBr) $\nu_{C=O}$ [cm^{-1}]
2a	C_6H_5	85	see experimental procedure		
2b	3-H_3C—C_6H_4	83	40–42°	C_8H_7BrOS (231.1)	1685
2c	4-H_3C—C_6H_4	83	25–27°	C_8H_7BrOS (231.1)	1705
2d	3-Cl—C_6H_4	81	83.5–85°	$C_7H_4BrClOS$ (251.5)	1689
2e	4-Cl—C_6H_4	77	49–51°	$C_7H_4BrClOS$ (251.5)	1680; 1693
2f	4-H_3CO—C_6H_4	86	40–41°	$C_8H_7BrO_2S$ (247.1)	1668; 1686

[a] Decomposition.
[b] Satisfactory microanalyses obtained: C ±0.28, H ±0.37.

Received: July 2, 1982

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[1] Since in 1952, no isolation of acylsulfenyl chloride except for acetylsulfenyl chloride by Böhme and Clement has been reported: H. Böhme, M. Clement, *Justus Liebigs Ann. Chem.* **576,** 61 (1952).
Acylsulfenyl iodides: S. Kato, E. Hattori, M. Mizuta, M. Ishida, *Angew. Chem.* **94,** 148 (1982); *Angew. Chem. Int. Ed. Engl.* **21,** 150 (1982).

[2] Only *in situ* generated chlorocarbonylsulfenyl bromide has been reported: W. Weiss, *British Patent* 1 132 108 (1968).

[3] M. Mizuta, T. Katada, E. Itoh, S. Kato, K. Miyagawa, *Synthesis* **1980,** 721.

[4] S. Kato, H. Watarai, T. Katada, M. Mizuta, K. Miyagawa, M. Ishida, *Synthesis* **1981,** 370.

[5] S. Kato, E. Hattori, H. Sato, M. Ishida, M. Mizuta, *Z. Naturforsch.* [b] **36,** 783 (1981).

[6] S. Kato, T. Mitani, M. Mizuta, *Int. J. Sulfur Chem.* **8,** 359 (1973).

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